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THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT MODERATELY LOW PRESSURES

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1. *Introduction.*—At moderately high pressures, the decomposition of gaseous nitrogen pentoxide was shown by the original work of Daniels and Johnston[1] to be homogeneous and of the first order and this has been completely confirmed by the work of subsequent investigators.[2] At low pressures, however, there has been a striking lack of agreement as to the rate of decomposition of this substance.

Hirst and Rideal,[3] Hibben,[4] and Loomis and Smith[5] have all tried to follow the rate of the decomposition at low pressures by freezing out the nitrogen oxides during the course of the reaction and measuring the pressure of the oxygen which had been formed. Working at initial pressures in the range 0.035–1.450 mm. of mercury Hirst and Rideal report that the specific rate of decomposition becomes greater at low pressures, the increase in rate being appreciable at 0.25 mm. and several fold at their lowest pressures. Hibben, on the other hand, working in the pressure range 0.03 to 0.18 mm. finds throughout the same specific rate of decomposition as at high pressures. Loomis and Smith, however, conclude that the method used in all three sets of experiments is unreliable, since, in the first place, they find that appreciable amounts of oxygen can be occluded and carried down with the condensed oxides of nitrogen, and in the second place, find that nitrogen pentoxide is appreciably adsorbed on the surface of pyrex glass.

More recently Sprenger[6] has attempted to follow the rate of decomposition by pressure measurements made with a quartz fibre gauge. Working in the range 0.01 to 0.05 mm. pressure, he comes to the extraordinary conclusion that the nitrogen pentoxide decomposes at approximately its high-pressure rate when it is first introduced into the reaction flask, and later, with a considerable fraction of the original nitrogen pentoxide still remaining, it ceases to decompose at all.

Finally, Rice, Urey and Washburne[7] report that preliminary measure-

ments made by Miss E. Wilson show that the specific rate of decomposition of nitrogen pentoxide falls below the high-pressure rate even at pressures of several millimeters.

Since the low-pressure rate of homogeneous gas reactions is of great theoretical interest, especially in connection with the theory of activation by collision as developed by Rice and Ramsperger[8] and by Kassel,[9] further work on the low-pressure rate of decomposition of nitrogen pentoxide seems desirable in view of the almost complete lack of agreement in the results described above.

2. *Special Features of the Present Experimental Method.*—In selecting an experimental method for the present work, special attention was paid to the elimination or minimization of the possible sources of error which appeared to us as most dangerous in work of this kind.

The possibility of occlusion of oxygen and the recurring disturbance in the condition of the decomposing gas, which occur when the reaction is followed by periodically freezing out the oxides of nitrogen and measuring the pressure of the residual oxygen, were eliminated by arranging to follow the course of the reaction by a direct measurement of the total pressure. This was accomplished by the use of a modified form of the "click" gauge originally devised by Smith.[10] The essential part of this gauge consists of a thin bulb of glass with a flattened side or diaphragm containing a wrinkle which produces a small clicking sound when the pressure difference on the two sides of the bulb is adjusted to a point where an inward or outward motion of the diaphragm occurs. The modifications introduced to make the gauge suitable for our low pressures consisted, (*a*) in making the diaphragm extremely thin so that the "click constant" or pressure difference necessary to operate the gauge was not too large compared with the pressures that were to be measured, (*b*) in attaching a microphone button on the tube leading to the gauge which made it possible to hear the click in a telephone receiver, and (*c*) in arranging a McLeod gauge to measure the small external pressure when the gauge clicked. The pressure readings thus obtained appeared to be reliable to about 0.01 mm. of mercury.

The dangers arising from the adsorption of gases on the walls of the reaction vessel were minimized in the following way. In the first place, we reduced the ratio of surface to volume by using an extraordinarily large reaction vessel, which was constructed from a 45-liter glass flask. In the second place, we cleaned the inside surface of the flask solely by wiping with a clean towel, and allowed *no* cleaning solution or other liquid to come in contact with it.[11] Finally, before each set of runs, the flask was heated to about 70°C. and pumped to a high vacuum before use, and furthermore before each set of runs nitrogen pentoxide was introduced into the flask and pumped out in order to condition the surface.

In addition to the dangers of adsorption on the surface, we also recog-

nized that the actual collision of molecules with the surface may be undesirable in producing an abnormal amount of molecular activation or deactivation as compared with that arising in the interior of the reacting mixture from the mutual collisions of the gas molecules themselves. This was an additional reason for going to the unusually large reaction vessel.

3. *The Apparatus and Experimental Procedure.*—The reaction was carried out as stated above in a 45-liter flask. This flask was placed in a specially constructed air thermostat, with suitably lagged walls and cover, and provided with air circulation and heating coils. The temperature was held constant throughout each run to within 0.05°C., but showed by soundings a maximum variation of 0.2 to 0.3°C. between different parts of the thermostat. This variation was allowed for by averaging and the final figures given are believed to be reliable to about 0.1°C.

The flask available was made of soft glass and was provided with a short "ring neck" about 4″ in diameter, the reinforced ring being approximately $^1/_2$″ thick and ground to a flat surface. The closing of the flask was effected by the use of a cap of plate glass, $^3/_8$″ thick, which was ground against the flat surface of the ring, while a 1″ glass tube leading to the "click gauge" and auxiliary apparatus was ground into a taper hole in this cap. The two ground glass joints were made tight by painting on the outside under vacuum with "Duco" lacquer. The bright red color of this material permitted us to determine the extent to which the lacquer had "crept" into the ground glass joints, and this did not appear sufficient to be serious.

The reaction flask was connected directly to the "click gauge" and through a stopcock to a smaller "fore flask" of a suitable size for containing the sample of pentoxide to be used. This "fore flask" was connected through stopcocks to a side trap containing the supply of solid pentoxide, to mercury diffusion pumps protected by a trap for freezing out mercury vapor and oxides of nitrogen, and to a McLeod gauge which could be used in the absence of nitrogen pentoxide for a direct measurement of the pressure in the reaction flask. The stopcocks were lubricated with a special high vacuum preparation.[12]

The nitrogen pentoxide was prepared from ozone and nitrogen dioxide, dried by passage through phosphorous pentoxide, and was condensed out in the side trap already mentioned, which was then sealed off from the preparation train and kept immersed in ice water. Samples of pentoxide were introduced into the reaction flask by first pumping the supply of condensed pentoxide free from its decomposition products, and then allowing evaporation to take place into the previously evacuated "fore flask," followed by admission into the evacuated reaction flask.

Before each run and in some cases after the run, the "click constant" or pressure difference necessary to operate the "click" was determined with

a high vacuum on the reaction side of the "click gauge" diaphragm. In case of a difference, the "click constant" determined before the run was used for correcting the pressures measured during the run, and the "click constant" determined after the run was used for correcting the final pressure. This difference was 0.03 mm. in the worst case.

At the end of the runs, a slight grayish deposit was found on the inside surface of the reaction flask. We believe this to have been produced from mercury vapor which in spite of our precautions must have entered the flask. It does not appear to have affected the constancy of our results.

TABLE I

Run No. 1. Temperature = 37.30°C. Click constant = 4.200 mm.

TIME SECONDS	PRESSURE ON McLEOD MM.	PRESSURE IN REACTION FLASK MM.	PRESSURE OF N_2O_5 MM.	SPECIFIC REACTION RATE $k(\text{SEC.}^{-1}) \times 10^4$
0				
110	6.244	2.044	0.826	
390	6.280	2.080		1.77
980	6.420	2.220	0.708	
1626	6.518	2.318		1.74
2310	6.636	2.436	0.562	
2980	6.732	2.532		1.65
3670	6.802	2.602	0.449	
3978	6.836	2.636		1.71
4770	6.916	2.716	0.372	
5696	7.004	2.804		1.62
6580	7.056	2.856	0.277	
6790	7.080	2.880		1.70
7850	7.154	2.954		
8988	7.192	2.992	0.184	
10980	7.268	3.068		
15570	7.354	3.154		
20670	7.412	3.212		
∞	7.460	3.260	0.000	
			Av.	1.70
			Mean deviation	0.04

4. *Experimental Results.*—Using the apparatus described above, 12 runs were made on the rate of decomposition of nitrogen pentoxide. Of these, Run 2 was not carried to completion since the data obtained showed a large total pressure of gas with only a small proportion of pentoxide. Run 5 was discarded because the reaction vessel had contained air before the run and the surface had not been conditioned by pumping out at a *high* temperature and by admitting and pumping out a preliminary charge of pentoxide, as was done in all other cases after the vessel had contained air. It gave a high "constant" which fell off during the run. Finally, Run 6 was discarded because of failure to obtain a sufficient quantity of pentoxide to measure with any accuracy.

To give an idea of the course of the 9 successful runs, we present below, in tabular form, the complete data for our highest pressure Run 1 in which the agreement of the different constants among themselves is good, and our lowest pressure Run 10, in which the agreement is necessarily much less good. Run 1 was carried out with material which had been only once condensed and presumably consisted originally of a mixture of pentoxide and dioxide, as shown by comparing the first measurement of total pressure with the pressure of pentoxide present. Run 10 on the other hand was carried out with material resublimed in a stream of ozone which gave us pure pentoxide, as indicated by the approximate check between the first measurement of total pressure and the pressure of pentoxide present.

TABLE II

Run No. 10. Temperature = 30.94°C. Click constant = 0.870 mm. (new diaphragm)

TIME SECONDS	PRESSURE ON McLEOD MM.	PRESSURE IN REACTION FLASK MM.	PRESSURE OF N_2O_5 MM.	SPECIFIC REACTION RATE k(SEC.$^{-1}$) $\times 10^4$
0				
215	1.060	0.190	0.1924	1.06
1183	1.088	0.218	0.1737	1.07
1850	1.106	0.236	0.1617	
2830	1.120	0.250		0.68
4070	1.140	0.270	0.1390	
5320	1.164	0.294		0.82
6740	1.181	0.311	0.1116	
8675	1.203	0.333		0.73
10950	1.225	0.355	0.0822	0.78
14400	1.254	0.384	0.0628	
17690	1.275	0.405		0.59
21425	1.286	0.416	0.0414	
58080	1.326	0.455		
∞	1.348	0.478	0.0000	
			Av.	0.818
			Mean deviation	0.141

The successive columns of the tables give the time in seconds measured from the instant when the reaction flask was closed off, the pressure necessary to operate the "click" as measured by the McLeod gauge, the total pressure in the reaction flask, the calculated pressure of pentoxide, and values of the specific reaction rate corresponding to the intervals indicated. The pressure in the reaction flask was obtained from the reading of the McLeod gauge by subtracting the "click constant." The pressure of pentoxide present at any time was calculated from the final pressure, making a correction for the degree of association of nitrogen dioxide to tetroxide, which was very small at these low pressures. The specific reaction rates were calculated on the basis of first order decomposition for intervals so chosen as to give a fair picture of the course of the reac-

tion. This was done by dividing the run into a reasonable number of intervals (5–9) in which approximately equal increases in pressure occurred. The first pressure reading was not used in three cases, since it did not fall on the smooth curve. This may have been due to haste in trying to adjust for the click. The interval method of calculation was chosen since it gives a fairer idea of any trend in the reaction even though it gives a poorer check among the constants. In no case was there any evidence of a trend in the reaction rate, except for the apparent trend in Run 10, which presumably is due to the inaccuracies of measurement in this very low-pressure run.

A summary of the final results for all 9 runs is given in the last table which is self-explanatory. In Runs 1–4, we used material which had been only once condensed and consisted of a mixture of pentoxide and dioxide as indicated by the first pressure measurement. In all the other runs, however, we used resublimed material and obtained in every case an approximate check between the first pressure measurement and the calculated pentoxide present at the start.

SUMMARY OF RESULTS

RUN NO.	TEMP. °C.	INITIAL PRESSURE IN FLASK MM.	NO. CONSTANTS CALCULATED	AVERAGE RATE CONST. (SEC.$^{-1}$) $\times 10^4$	MEAN DEVIATION	HIGH PRESSURE RATE CONSTANT (SEC.$^{-1}$) $\times 10^4$
10	30.94	0.190	7	0.818	0.141	0.775
12	30.76	0.789	7	0.736	0.056	0.757
11	30.76	0.890	9	0.739	0.049	0.757
4	36.84	0.380	8	1.57	0.32	1.70
3	36.80	0.884	8	1.56	0.13	1.68
1	37.30	2.044	6	1.70	0.04	1.79
9	41.97	0.397	5	3.11	0.41	3.25
7	41.98	0.700	8	3.31	0.18	3.25
8	42.00	0.710	8	3.17	0.23	3.25

5. *Conclusion.*—For comparison we have given in the last column of the final table the *high pressure* rate of decomposition of nitrogen pentoxide, as obtained from the data of Daniels and Johnston, by taking the best straight line through a plot of their values of log k against $1/T$ for the temperatures 25°, 35°, 45°, 55° and 65°. The agreement between our constants and theirs is probably within the experimental error of either piece of work.

We may conclude that, down to the pressure range that we have investigated, nitrogen pentoxide shows no change in its specific first-order rate of decomposition. It should be particularly noted that there is no falling off in the rate, in contradiction to the preliminary result of Miss Wilson of a falling-off at pressures of several millimeters, as reported by Rice, Urey and Washburn.

The behavior at still lower pressures is a matter of great interest. We

hope to obtain data on this in the near future by using a different method of pressure measurement.

[1] Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).

[2] For a bibliography of experimental work on nitrogen pentoxide, and tests of the constancy of high pressure rate, see Rice and Getz, *J. Phys. Chem.*, **31**, 1572 (1927).

[3] Hirst and Rideal, *Proc. Roy. Soc.*, **109A**, 526 (1925).

[4] Hibben, *J. Am. Chem. Soc.*, **50**, 940 (1928).

[5] Loomis and Smith, *J. Am. Chem. Soc.*, **50**, 1864 (1928).

[6] Sprenger, *Zeit. physik. Chem.*, **136**, 49 (1928).

[7] F. O. Rice, Urey and Washburn, *J. Am. Chem. Soc.*, **50**, 2402 (1928).

[8] O. K. Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927); *Ibid.*, **50**, 617 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 113, 118 (1928).

[9] Kassel, *J. Phys. Chem.*, **32**, 225 (1928); *Ibid.*, **32**, 1065 (1928).

[10] D. F. Smith and Taylor, *J. Am. Chem. Soc.*, **46**, 1393 (1924).

[11] The flask was taken from stock but as far as we are aware had not previously had liquid in it.

[12] Obtainable from Metropolitan Vickers Electric Co., Ltd., Strafford Park, Manchester, England.

TYPES OF UNIMOLECULAR REACTIONS

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Recently certain writers have expressed the belief that chemical reactions are to be explained on the basis of the quantum mechanical resonance phenomenon.[2] There are a large variety of different types of chemical reactions, of different degrees of complication, some of which may be too complicated to treat directly by quantum mechanical methods, but some of which are so simple that they have already been treated in more or less detail on the basis of the new mechanics. In this situation it seems desirable to point out the relations between certain reactions, one of which has been considered on the basis of the quantum mechanics, and the others of which have been treated only by classical or old quantum theory methods. We hope later to consider some of these relations in more detail with a view to seeing whether we can make new inferences (even though they must necessarily be of a preliminary nature) about the more complicated reactions.

The types of reaction which we wish to consider are predissociation, unimolecular decompositions of complex organic compounds, and photochemical decomposition of the same compounds, all occurring in the gaseous state.

1. *Predissociation.*—Predissociation can occur when a molecule can